# Industrial applications of multi-functional, multi-phase reactors

Harmsen, G.J.; Chewter, L.A.

*Published in:*
Chemical Engineering Science

*DOI:*
10.1016/S0009-2509(99)00082-2

PERGAMON

Chemical Engineering Science 54 (1999) 1541-1545

Chemical Engineering Science

# Industrial applications of multi-functional, multi-phase reactors

G.J. Harmsen and L.A. Chewter

Shell International Chemicals, Shell Research and Technology Centre, Amsterdam, The Netherlands

**Abstract** - To reveal trends in the design and operation of multi-functional, multi-phase reactors, this paper describes, in historical sequence, three industrial applications of multi-functional, multi-phase reactors developed and operated by Shell Chemicals during the last five decades. For each case, we describe the design requirements, the design knowledge that was used and how the reactor was designed conceptually. In addition, we also indicate what development methods, models and tools were applied, and how commercial start-up and operation went.

Due to an increased demand for processes that produce no waste, require little energy, are low in cost and produce products of excellent quality, it is expected that more multi-functional reactors will be developed and operated in future. These reactors will be conceptually designed using increasingly systematic methods, in which all requirements - Safety, Health and Environment, Sustainability, Product Quality and Low Cost - are first translated into functions. Requirements are thus combined as much as possible on a functional level after which the appropriate equipment is designed. Reliable start-up and operation will be increasingly achieved by the modelling of all individual functions and integration of these functions into comprehensive reactor models together with well designed, small-scale experiments. 

*Keywords:* Multi-functional, Multi-phase Reactors, Chemical Reaction Engineering, Reactor Modelling, Process Synthesis, Health, Safety and Environment, Sustainable Technology.

## INTRODUCTION

In the first two decades following the Second World War, markets for new consumer products were growing rapidly. The chemical industry was a major provider of the materials for these products, such as plastics and resins. The main emphasis in process design and development was on quick development and large scale production facilities. Chemical Reaction Engineering, now emerged as a distinctive skill, was benefiting from the tremendous increase in the power and programming ease of computers and was beginning to impact on the design and development methods.

Since 1980, the effects of large-scale industrialisation on depletion of scarce natural resources have become apparent. Furthermore, consumers have wanted higher product quality (less deviation from target) and market globalisation has increased competition. Hence demands for improvements in Health, Safety and Environment (HSE), for sustainable processes, a higher product quality as well as economic drivers have increased enormously the requirements on process design. In this period we have also seen Process Synthesis emerge as a distinctive discipline, providing explicit knowledge on how to generate new process designs meeting all demands.

To reveal the effects of these changes on the design and operation of the multi-functional multi-phase reactor, we describe, in historical sequence, three industrial applications of such reactors, developed and operated by Shell Chemical during the last five decades. For each case, we describe the design requirements, what design knowledge was used and how the reactor was designed conceptually. In addition, we also indicate what development methods, models and tools were applied, and how commercial start-up and operation went.

## REACTIVE DISTILLATION

### *Reactor System Description*

The reaction scheme is as follows:

$$A + B \rightarrow P + \text{salt} \qquad (1)$$

$$P + B \rightarrow X \qquad (2)$$

The reactor, a reactive distillation system, is shown in figure 1.

The feed, component A, an organic chorine compound, is fed as an aqueous solution to the top part of the column. Component B, an alkali, is fed as an aqueous slurry. The alkali dissolves and reacts with A in the liquid phase to product, P. The desired product P is transferred to the gas phase. In this way the occurance of the consecutive reaction (2) is minimised. As A is also volatile, a top cooler and reflux is applied for sharp separation of P from A.

0009-2509/99/$-see front matter 
PII: S0009-2509(99)00082-2

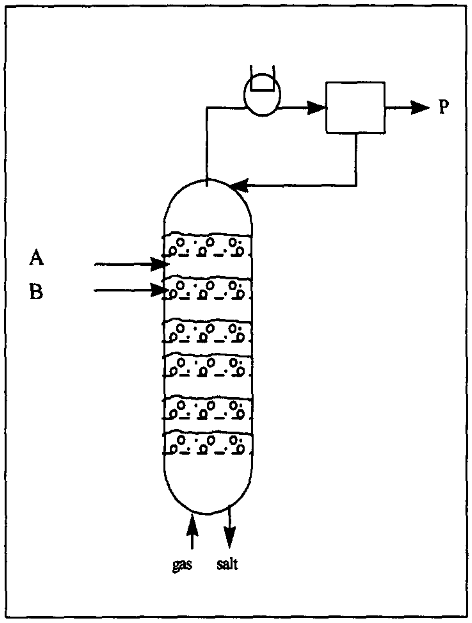


**Figure 1- Reactive distillation**

The functions combined in this reactor are:

- dissolution of alkaline
- reaction
- separation of P from reaction mixture

### *Historic Description from Reactor Conception to Reactor Operation*

The conceptual design of this reactive distillation reactor was carried out at Shell USA in the 1940's! Little could be found in the company's files on the designers' considerations leading to this concept. Distillation of product P from the reaction mixture was a known unit operation. Consecutive reactions of P were known qualitatively.

The development was spurred by the Second World War requiring the product. Oversizing of the liquid hold-up in the column was applied to ensure complete conversion of A. Extra by-product make from consecutive reactions was allowed in the first design phase.

The first start-up of the system was successful. During the first years of operation, by-product make was reduced by computer modelling of the reaction and mass transfer steps. This was one of the first applications of computer programming for process optimisation within Shell in the 1950's.

In decades to follow, the operation was steadily improved in capacity and product yield by more detailed modelling. Recently, all phases were modelled in detail for further optimisation of the operation, including optimisation of particle size feed requirements.

## PRECIPITATIVE/EVAPORATIVE REACTOR

### *Reactor System Description*

The reaction scheme is as follows:

$$A + B \rightarrow P + salt \qquad (3)$$

The reaction is exothermic. In total 14 by-product reactions are known. The main by-product reaction is:

$$P + A \rightarrow X \qquad (4)$$

All reactions take place in the liquid phase and all reactions are first order in the constituent components.

The reactor system consists of several gas-liquid-solid stirred tank reactors in series, as shown in figure 2.

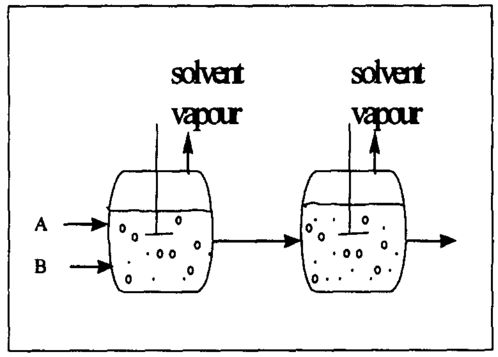


**Figure 2 - Evaporative/precipitate Reactor System**

The system combines the following functions:

- Mixing
- Reaction
- Solvent separation (by evaporation) from reaction mixture
- Salt separation (by precipitation) from reaction mixture
- heat exchange

### *Historical Description from Reactor Conception to Reactor Operation*

The conceptual design of the reactor system was derived in the early sixties as follows. From successful experience with a similar reaction system, the water solvent evaporation and salt precipitation during reaction in a stirred reactor were obtained. The advantages are that by-product make is minimised and that the separation of the salt from the product is done by simple L/S separation.

To reduce capital expenditure and operator cost, continuous operation was chosen. From reaction engineering theory, the choice for several reactors (staging), to minimise consecutive reaction was obtained.

The development was based on calculations with an analogue computer which were carried out by the late Jan van der Vusse to determine the optimum number of reactors and their size. An experimental small-scale reactor system was operated to obtain the reaction kinetic parameters for the model.

***Selection and Design of the Real Reactor System***

The reactor system selected was a number of mechanically stirred reactor in series. In each reactor, water evaporates in situ and is removed by a vapour outlet; hence the reactor system operates at very low water concentrations in the liquid reaction phase. Moreover, evaporation provides a cheap method of cooling.

***Development***

A small-scale pilot plant (litre scale) was operated successfully using the same number of reactors as the commercial design. Experimental results on by-product make were compared with the theoretical model. Some kinetic parameters were adjusted and an improved design was made.

***Commissioning and Start-up***

Start-up of the process was successful. Steady-state operation was achieved within only a few months. This compares favourably with the industry average start-up time prediction. Within a year, design capacity and selectivity were achieved and after 3 years the capacity was 114 % of the design capacity.

***Operation: Capacity and Product Quality Improvement***

In the years to follow, more comprehensive reactor models were made to support debottlenecking and product quality improvement. In the last decade, the reactor model was extended to included the full kinetics of all 15 by-products reactions. This model was then used to optimise conditions for robust operation, minimising variation in by-product formation, hence increasing the product quality.

Also, the salt precipitation was modelled to predict the particle size distribution in relation to reactor conditions. This model was then used to optimise the L/S separation . The model is steady-state and comprises particle nucleation and crystal growth kinetics derived from the literature. Parameter values were obtained by fitting with plant data.

***Summary of Reaction System***

A novel reactor system which combines 5 functions (mixing, reaction, evaporation, cooling, and precipitation) was successfully selected, developed, designed and started-up. Continuous improvement in capacity, by-product reduction and product quality was obtained by detailed understanding of the constituting functions and integrating these with comprehensive models.

## LIQUID-LIQUID EXTRACTION REACTOR

***Reactor System Description***

The main reaction is a reaction of an organic chloride (A) with an alkali (B) in solution,

$$A + B \rightarrow P + \text{salt} \tag{5}$$

The reactor system consists of a co-current, liquid-liquid, multi-stage mixer reactor, as shown in figure 3.

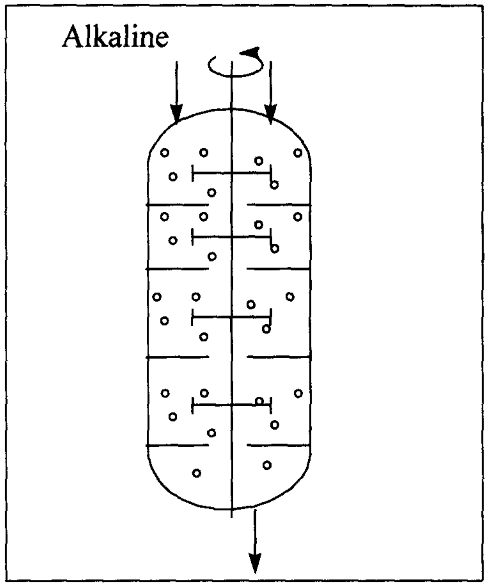


**Figure 3 - Liquid-liquid Extraction Reactor**

The functions combined in this reactor equipment are:

- liquid-liquid alkaline mass transfer to reaction phase
- reaction
- salt extraction from organic reaction to aqueous phase

***Historical Description from Reactor Conception to Reactor Operation***

The conceptual design was derived as follows. The choice of solvent for the reaction system and the multi-stage system was made by using the experience with a similar reaction in an existing plant and available detailed design knowledge for multi-stage, liquid-liquid extraction mixers within Shell. A first estimate on the number of stages, and the alkali to A ratio was made by assuming first order mass action kinetics.

The development was very short due to maximum use of in-house knowledge on multi-stage, mechanically-stirred extraction columns (derived from cold flow modelling) both for designing internals and stirrers for narrow residence time distribution and reliable liquid-liquid dispersion.

Furthermore, the development was based on extensive modelling of both mass transfer and reaction kinetics. Experimental Design methods were applied to define batch experiments for the determination of both kinetics and the mass transfer parameters. No pilot plant was built.

The final design was optimised with the main emphasis on product quality, defined as minimum variation in the product specification. A parameter design method, derived by the author (Harmsen, G.J. 1996a,b) was applied to obtain maximum robustness to process disturbances. This avoided the use of a complex process instrumentation and control system.

Robust start-up conditions were defined as well as Statistical Process Control corrective actions, both based on the reaction model. Extensive training sessions with operators were also organised. Furthermore, the equipment was tested for its residence time distribution by pulse salt injection and conductivity measurements.

Start-up was very successful. Design capacity was reached within 14 days, while meeting product quality requirements.

## PAST TRENDS IN INDUSTRIAL APPLICATIONS OF MULTI-FUNCTIONAL REACTORS

The cases presented in the last three sections illustrate the development of methodologies for the design and development of multi-functional, multi-phase reactors, which have been applied in the chemical industry for at least five decades.

The conceptual design of these reactors was, in general, carried out by experienced chemical engineers who used knowledge from equipment applications in other processes; i.e., by using experience rather than a comprehensive modelling approach. The main driver was to minimise the number of process operations and the size of the reactor.

A clear trend in the design stage of the processes was the increased use of modelling, and, in particular, the use of computers when they became available. Comprehensive modelling has also been applied to existing systems to improve operation.

In early designs, reliable scale-up was obtained by using pilot plant experiments in combination with a conservative design, allowing in the first period of operation some excess by-product make (see first two examples). More recently, the need to go through the pilot-plant stage has often been obviated by the use of more comprehensive models in combination with specifically designed experiments on a laboratory scale (see last example).

The designs have over time become less conservative and a better prediction and control of by-product make has been achieved. It has even been possible to build in robustness at the design stage to reduce costs in the control system.

## CURRENT TRENDS IN INDUSTRIAL APPLICATIONS OF MULTI-FUNCTIONAL REACTORS

For two reasons we think that multi-functional reactors will be applied more in the future. The first is the increased demands on process designs; the second is increasing availability of design methods and the supporting tools.

Safety, Health and Environmental requirements and the drive for Sustainable development - the so-called SHES criteria - are placing ever increasing demands on new processes (Shell Chemicals, 1998). A comprehensive description of the demand for sustainable chemical technology is provided by Lemkowitz (Lemkowitz, Harmsen and Nugteren, 1998). Some possible effects of the sustainability demand and others on the applications of multi-functional reactors are illustrated in the following.

The consumption of primary fossil fuel per unit product must decrease considerably to avoid further build up of $CO_2$ in the atmosphere in view of the increased risk of global climate changes. As every process step is irreversible, it loses exergy. By applying multi-functional reactors, i.e. by combining more functions in one piece of equipment, the number of process steps reduces and so in general the exergy loss will reduce; hence primary energy consumption per unit product will reduce.

The environmental burden caused by the chemical industry, due to waste production, should also be reduced. In many multi-functional reactors, the by-product make can reduced by *in-situ* removal of product from the reaction phase; hence reducing waste production caused by consecutive reactions.

Due to globalisation, the competition in the chemical industry is more fierce than ever, demanding lowest cost of operation. Again, application of multi-functional reactors will, in many cases, mean lower capital investment and lower variable cost, due to less equipment installed and a more optimised operation.

Development of conceptual design methods has increased greatly the last decade both in academic and in industrial institutes; see for instance publications by Harmsen (Harmsen and van Hulst, 1998; Siirola, 1995; and Schembecker, 1994). It is likely that this development will speed up in the next decade. These design methods enhance the creativity of the process designer to invent new reactor designs, combining as many functions in one piece of equipment as possible and thereby meeting more stringent demands from environmental legislation, on product quality and process economics. Moreover, the capability of simulation tools, both steady state and dynamic, are increasing continually. Conceptual design options are thereby more easily evaluated. An overview of process simulation tools capability is provided by Harmsen (Harmsen, 1996c). This also enhances creativity, as this allows more options to be generated for evaluation.

Development of new designs can also be more rapid because of these comprehensive modelling tools in combination with well designed laboratory scale experimental set-ups to validate the models. In this way, in many cases a demonstration-scale intermediate step can be avoided.

The ultimate goal of multi-functional, multi-phase reactors is of course to incorporate the whole process in a single piece of equipment. This has already been achieved commercially by Eastman Chemicals for their methylacetate process (Siirola, 1995). It is, therefore, expected and desired that more multi-functional, multi-phase reactors will be developed and operated in the future.

## CONCLUSIONS

- Multi-functional, multi-phase reactors have been applied in the chemical industry for at least the last five decades.
- The main driver in the past was the desire to minimise the number of process operations and the size of the reactor.
- Reliable design in the past was obtained by modelling essential elements in combination with conservative sizing.
- Operation is continuously improving by the increased availability of comprehensive modelling capabilities.
- Multi-functional, multi-phase reactors will be applied more in the future due to increased demand for processes that meet more stringent requirements from society on Safety, Health Environment, Process Sustainability, Product Quality and Low Cost.
- New methods (process synthesis) are appearing that aid the designer in generating new multi-functional, multi-phase reactor designs which meet all these requirements.

## REFERENCES

Harmsen, G.J., 1996a Product Quality at lowest Cost: Robust Processes by Parameter and Tolerance Design Using Integration Tools. *Proc. Sec. Int. Conf. Computer Integrated Manufacturing in the Process Industries, Eindhoven 1996,* 293-297.

Harmsen, G.J., 1996b Perfecting the parameters. *Chem. Proc. Techn. Int.* No. 8, 148-155.

Harmsen, G.J., 1996c At the touch of a key. *Chem. Proc. Techn. Int.* No. 8, 143-146.

Lemkowitz, S.M., Harmsen and G.J., Nugteren, H.W., 1998 The Challenge of Sustainable Development to Chemical Engineering: A new Paradign for the 21st Century?, key note lecture. *AIChE Fall meeting 1998, Miami USA.*

Harmsen, G.J., and van Hulst, H., 1998 Reactor Selection Methodology. *CAPE symposium Process Synthesis; Art and Application, 3 February 1998 Amsterdam.*

Siirola, J.J., 1995 An industrial perspective on process synthesis. *4th Int. Conf. Foundations Computer-aided Process Design, AIChE Symp. Series* Vol. 91, No. 304, 222-233.

Shell Chemicals, 1998 A world of chemicals. *Information handbook 1998/99.*

Schembecker G. et.al., 1994 Synthesis of chemical process flowsheets by means of cooperating knowledge integrating systems. *Escape 4, 4th Eur. Symp. Computer Aided Process Engineering, Dublin.*